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Analytical Studies of Some Acyloin-Oximes.

Hans A. Suter
Louisiana State University and Agricultural & Mechanical College

ANALYTICAL STUDIES OF SOME ACYLOIN OXIMES

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Hans Albert Suter
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ABSTRACT

The purpose of the present investigation was to examine the behavior of the copper (II) salts of the α-isomers of some acyloin oximes towards a series of selected amines in order to explain the unusual solubility relationships which these copper salts exhibit towards ammonium hydroxide. The insolubility in ammonium hydroxide of copper salts of acyloin oximes has been attributed to their being inner complex salts in which aromatic or multimembered aliphatic radicals serve as coordination centers for the copper ion. Evidence is presented which makes coordination to these radicals seem rather improbable. Based on the solubilities of the copper (II) salts studied, a polymeric structure for copper (II) acyloin oximes is proposed.

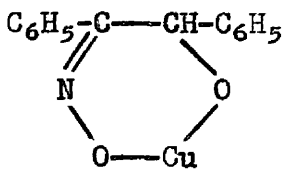
The study included the following α-isomers of acyloin oximes: benzoin oxime, 2,2'-furoin oxime, phenylbenzoin oxime, methylbenzoin oxime, 2,2'-thenoin oxime, α-hydroxyisobutyrophenone oxime, and α-hydroxyacetophenone oxime. With the exception of benzoin oxime, none of the above compounds had been investigated from the standpoint of their possible use in analytical chemistry.

It was found that as a precipitant for copper, benzoin oxime is superior to any of the compounds tested. However, α-hydroxyisobutyrophenone oxime and α-hydroxyacetophenone oxime are superior to benzoin oxime as qualitative reagents for copper (II) ions.

INTRODUCTION

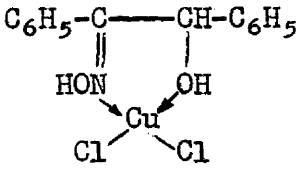
Benzoin oxime was proposed by Feigl[13] as a specific reagent for copper (II) ions in ammoniacal solution. The reagent is suited not only for the qualitative detection of copper, but also for the quantitative determination of this element. With copper (II) ions, the α-isomer of benzoin oxime, C_6H_5-C(NOH)-CH(OH)-C_6H_5, forms a dark green, flocculent precipitate, which is insoluble in water and dilute ammonium hydroxide, as well as in most organic solvents. An exception is chloroform, in which the copper salt is somewhat soluble[23]. Dilute aqueous mineral acids, however, readily decompose the green salt. In this connection it is interesting to note that the decomposition does not result in the formation of benzoin oxime and the copper (II) salt. Instead, benzoin oxime is cleaved in acidic solution into benzoin and the hydroxylammonium ion. The hydroxylamine salt reduces the intermediately formed copper (II) ion to the respective copper (I) salt. Therefore, copper (I) chloride is obtained when copper (II) benzoin oxime is decomposed by aqueous hydrochloric acid[21].

Elemental analysis established that the ratio of copper to benzoin oxime is 1:1. Consequently, copper (II) ion replaces not only the hydrogen of the oxime group, but also the hydrogen atom of the alcoholic hydroxyl group. Based on the analytical results, the structure of the copper salt of benzoin oxime was given by Feigl[13] as:



Jennings, Sharratt and Wardlaw[21] noted that it was unusual for the

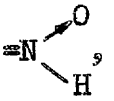
hydrogen of a secondary alcoholic group to be replaced by copper. Because benzoin oxime is a reducing agent, one could expect it to reduce the copper (II) ion to copper (I) ion resulting in the formation of a green copper (I) salt. Manifestly, benzoin is readily oxidized by copper (II) salts in pyridine solution, and use is made of this reaction for the preparation of benzil from benzoin[15]. Jennings and coworkers[21] discovered, however, convincing evidence that the green salt, which is obtained by the action of benzoin oxime upon copper (II) ion, is, indeed, a copper (II) salt. By treating copper benzoin oxime with alcoholic hydrochloric acid, they were able to isolate a green crystalline material which had the following structure:

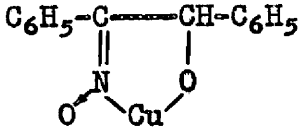


This compound could not have been obtained, if the copper benzoin oxime had been a copper (I) salt.

Additional evidence for the bivalency of copper in copper benzoin oxime was obtained in the course of this investigation. If copper (II) ions would oxidize benzoin oxime, the oxidation product should be benzil monoxime. Therefore, by a suitable method of decomposition of the green copper benzoin oxime, benzil monoxime should be obtainable, provided a reduction of copper ion had occured. It was found that an aqueous suspension of copper benzoin oxime is decomposed by hydrogen sulfide with the formation of copper sulfide together with the consequent release of the organic complex former. The organic component was extracted with ether and the extracted compound identified as benzoin oxime by its melting point. Because the copper benzoin oxime used in this experiment was precipitated from a solution which contained

excess copper (II) ion, all benzoin oxime could be expected to be oxidized, if this oxidation were to occur at all.

In view of this evidence it can be considered as established that copper benzoin oxime is the salt of divalent copper. There remains, however, the question, whether the chelate ring is five- or six-membered. At the present, there is no proof available to decide this question. But in analogy with the structure of nickel salts of α-dioximes[36], where it has been proven that the salinogenic oxime group reacts in its tautomeric nitrone form,  , the structure of the copper salt of benzoin oxime should be written as:



This latter structure is probably the correct one and Feigl[11] has adopted it.

Because the copper salt of benzoin oxime is generally not soluble, and especially because of its insolubility in dilute aqueous ammonium hydroxide, Feigl[13] postulated it to be an inner complex salt.

By definition, an inner complex salt is a neutral chelate compound in which the coordination number and charge of a metal ion is exactly balanced by the sum of the donor atoms and charges, respectively, of the chelating molecule with which it combines[25]. The bonds between the metal ion and the chelating agent are covalent. Therefore, two requirements must be fulfilled for atoms to function as donors or coordination centers for a metal ion:

a) They must possess an unshared pair of electrons.

b) Their position with respect to the salinogenic groups must be such that a more or less strain-free ring containing the metal ion can be formed.

To the covalent bonding, enhanced by the formation of rings, is ascribed the

chemical stability as well as the physical properties which characterize chelates in general and inner complex salts in particular.

Benzoin oxime is not unique in its ability to form green, water insoluble copper salts. As has been shown by Feigl, Sicher and Singer[14], it is likely that all α-oximes of acyloins share this reactivity towards copper (II) ions. Table I gives the oximes prepared and studied by these authors. They found that all these compounds formed green, water insoluble copper salts in which the ratio of copper to organic component is 1:1. The green copper salts, however, show differential behavior towards dilute ammonium hydroxide. As can be seen from Table I, insolubility in dilute ammonium hydroxide appears with aliphatic acyloin oximes which are derived from aldehydes containing more than four carbon atoms. All copper salts of aromatic acyloin oximes, with the exception of phenyl- and benzyl-derivatives of benzoin oxime, are insoluble in dilute ammonium hydroxide. Feigl and coworkers (loc. cit.) consider the ammonium hydroxide insoluble copper salts as inner complex salts and ascribed to aromatic radicals, as well as to aliphatic radicals containing more than three carbon atoms, coordinative ability towards copper (II) ions.

Pfeiffer[35], however, does not consider the copper salts of aliphatic acyloin oximes as inner complex salts, but states that the copper salts of aromatic acyloin oximes might be regarded as having inner complex salt character in which the phenyl radicals serve as coordination centers for the copper (II) ion.

To substantiate the coordinative ability of aromatic groups, both Pfeiffer and Feigl and coworkers cite the crystalline substances of aromatic compounds such as benzene, thiophene, furane, pyrrole, aniline and phenol which are formed when these compounds are shaken with an ammoniacal solution

Table I

ACYLOIN OXIMES STUDIED BY FEIGL AND COWORKERS

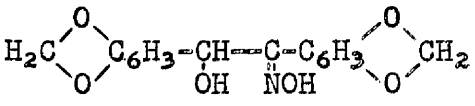
Name of compound	Formula of compound	Behavior of Cu-salt towards dilute NH_4OH
Fructose oxime	$HOCH_2-\underset{\underset{NOH}{\|}}{C}-(CHOH)_3CH_2OH$	soluble
Acetol oxime	$HOCH_2-\underset{\underset{NOH}{\|}}{C}-CH_3$	soluble
Acetoin oxime	$CH_3-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-CH_3$	soluble
Proprioin oxime	$C_2H_5-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_2H_5$	soluble
n-Butyroin oxime	$C_3H_7-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_3H_7$	soluble
n-Valeroin oxime	$C_4H_9-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_4H_9$	insoluble
n-Caproin oxime	$C_5H_{11}-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_5H_{11}$	insoluble
Enanthoin oxime	$C_6H_{13}-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_6H_{13}$	insoluble
Phenylacetoin oxime	$C_6H_5CH_2-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-CH_2C_6H_5$	insoluble
Benzoin oxime	$C_6H_5-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_6H_5$	insoluble
Furoin oxime	$C_4H_3O-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_4H_3O$	insoluble
4,4'-Dimethoxy-benzoin oxime	$H_3COC_6H_4-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_6H_4OCH_3$	insoluble
4,4'-Diisopropyl-benzoin oxime	$(CH_3)_2CHC_6H_4-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{NOH}{\|}}{C}-C_6H_4CH(CH_3)_2$	insoluble
Piperoin oxime		insoluble

Table I (contd.)

Name of compound	Formula of compound	Behavior of Cu-salt towards dilute NH_4OH
∝-Hydroxyphenyl-acetamide oxime	$C_6H_5-\underset{OH}{CH}-\underset{NOH}{C}-NH_2$	difficultly soluble
Benzofuroin oxime	$C_6H_5-\underset{OH}{CH}-\underset{NOH}{C}-C_4H_3O$	insoluble
4'-Methoxybenzoin oxime	$C_6H_5-\underset{OH}{CH}-\underset{NOH}{C}-C_6H_4OCH_3$	insoluble
4-Isopropyl-4'-methoxybenzoin oxime	$(CH_3)_2CHC_6H_4-\underset{OH}{CH}-\underset{NOH}{C}-C_6H_4OCH_3$	insoluble
4-Dimethylamino-benzoin oxime	$C_6H_5-\underset{OH}{CH}-\underset{NOH}{C}-C_6H_4N(CH_3)_2$	insoluble
4-Dimethylamino-4'-chlorobenzoin oxime	$ClC_6H_4-\underset{OH}{CH}-\underset{NOH}{C}-C_6H_4N(CH_3)_2$	insoluble
Phenylbenzoin oxime	$(C_6H_5)_2-\underset{OH}{C}-\underset{NOH}{C}-C_6H_5$	soluble
Benzylbenzoin oxime	$C_6H_5CH_2 \diagdown \underset{C_6H_5 \diagup OH}{C}-\underset{NOH}{C}-C_6H_5$	soluble

of nickel cyanide. The empirical formulae of these crystalline substances are $Ni(CN)_2 \cdot NH_3 \cdot AC$, where AC represents the aromatic molecules. These interesting compounds were first observed and analyzed by Hofmann and collaborators[20] and later were regarded as coordination compounds between ammoniacal nickel cyanide and benzene, etc. Recently, however, Powell and Rayner[37] have demonstrated by X-ray studies that the compound $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ is a clathrate compound.

A clathrate is a type of molecular compound, CM, discovered by Palin and Powell[28] which is formed by the imprisonment of one molecule of one component, M, in some kind of cage structure of the other component, C. Although the composition of clathrate compounds appears to be stoichiometric, it has been shown that no chemical bond whatever exists between the encaging structure and the entrapped molecule. The only requirement which M has to meet in order to form a clathrate with C is that of size. M has to possess such dimensions as to fit into the cavities which exist in the cage structure C.

Because the "compound" between ammoniacal nickel cyanide and benzene has been shown to be a clathrate, no analogy regarding the coordinative ability of aromatic radicals can be drawn between the latter "compound" and copper benzoin oxime. Consequently, the findings of Powell and Rayner (loc. cit.) make coordination to phenyl radicals rather improbable.

The structural formula of benzoin oxime shows that two functional groups in the molecule, the oxime group and the hydroxyl group, could function either as salinogenic groups or donors for metal ions. As has been mentioned before, the copper salt of benzoin oxime results from the interaction of one molecule of benzoin oxime with one copper ion. Consequently, the two

groups function as salinogenic groups, the hydrogen atoms of these groups are replaced by a copper atom. This leaves no atom of benzoin oxime which contains an unshared pair of electrons for coordination to the copper atom. Feigl, Sicher and Singer (loc. cit.) postulate that the copper atom is not coordinated to any particular atom of benzoin oxime but to the phenyl radicals as a whole.

This postulate, however, has two weaknesses. First, the copper salts of acyloin oximes are the only representatives of this type of coordination. No other examples of substantiating evidence have been discovered to date. But this argument is not very convincing because in the future such type of coordination might be observed.

Secondly, the postulate of coordination to phenyl radicals in benzoin oxime meets with a contention which cannot be neglected. This contention is that of bond length. From a molecular model of benzoin oxime it can be seen that the distance between the copper atom and the phenyl radicals would be very great. Because of this large distance, any interaction between the copper atom and the phenyl radicals becomes extremely unlikely.

The explanation of the insolubility in ammonium hydroxide of copper benzoin oxime based on its being an inner complex salt meets with a further difficulty. From Table I, it can be seen that the copper salts of aliphatic acyloin oximes derived from aliphatic aldehydes of more than four carbon atoms are likewise insoluble in dilute ammonium hydroxide. Even if phenyl radicals were able to coordinate to copper, this property cannot be ascribed to saturated hydrocarbon radicals.

Saturated hydrocarbons are characterized by their great inertness towards chemical agents. Addition compounds involving saturated hydrocarbons

are not known. Forcradn[17] discovered some hydrocarbon hydrates which correspond to the general formula HC.$6H_2O$ where HC represents methane, ethane, propane, and isobutane. These "compounds" could be considered addition complexes of hydrocarbons, but they have been shown by von Stackelberg[42] to be clathrate-type compounds. Although this author does not call the hydrocarbon hydrates clathrates, he states clearly that for their formation the size and shape of the hydrocarbon molecule are the determining factors. The encaging structure in this case is the ice which contains the required cavities. As Powell and coworkers have demonstrated, this is a characteristic of clathrate compounds.

Unsaturated hydrocarbons, i.e. olefins, however, have been shown by Winstein and Lucas[47] to form complexes with silver ions under special conditions. The formation of addition complexes of olefins is not restricted to silver ions only. For example, ethylene undergoes a series of addition reactions with metal salts of which the compounds with platinum (II) chloride are the best known[32]. Not only ethylene but also higher homologous members of ethylene form addition complexes with metal salts[33]. Addition reactions to the ethylenic bond can best be interpreted by the formation of carbonium ions[2] according to:

$$-\overset{|}{C}::\overset{|}{C}- \;+\; H^+ \longrightarrow -\overset{|}{C}-\overset{|}{\overset{+}{C}}-H$$

Acetylenic compounds are even more reactive than olefins, and copper (II) and silver (I) ions are capable of compound formation with acetylene. The resultant metal acetylides are easily prepared, but when dry decompose explosively.

At first sight it might appear that the metal salt-olefin complexes would lend support to coordination to phenyl radicals. But it is well known that the conjugated double bonds of aromatic hydrocarbons possess only a

limited amount of ethylenic double bond character. Pauling[31] considers that the carbon-carbon bonds of benzene have only 50% double bond character. This conclusion is arrived at from the equivalence of the six carbon-carbon bonds of benzene. A consequence of this limited double bond character is the reactions peculiar to aromatic compounds. While unsaturated aliphatic compounds are generally easily oxidized and undergo as a rule a series of addition reactions, aromatic compounds are remarkedly stable towards oxidation and do not undergo addition reactions of the same type as ethylenic hydrocarbons. With antimony (III) halides, benzene and its homologues form products of the general formula $HC_6H_5 \cdot nSbX_3$, where n is 1 or 2[34]. These "compounds" have not been isolated and their existance was demonstrated from cooling curves. The assumption that addition products of aromatic hydrocarbons are formed is necessary in order to explain the mechanism of their substitution reactions. The existance of addition products of aromatic compounds, however, is only transitory.

The insolubility in aqueous ammonium hydroxide of the copper salts of certain acyloin oximes is, indeed, a rather unusual behavior of copper (II) salts. With the exception of copper (II) sulfide and complex copper (I) cyanide all copper salts, regardless of their solubilities in water, dissolve in ammonium hydroxide with the formation of tetrammine copper (II) ions. Even inner complex salts of copper (II), such as the copper (II) salts of 2,4-pentanedione, 8-quinolinol, etc., readily dissolve in aqueous ammonia. The explanation for the solubility of copper salts in aqueous ammonium hydroxide has to be sought in the strength of the bonds of the copper (II) tetrammine complex. The copper-nitrogen bond is very strong and therefore the ammonia complex is only very slightly dissociated in water. Practically all salts of copper dissociate to such a degree that the copper (II) ion concentration exceeds the

copper (II) concentration derived from the ionization product of the soluble copper (II) tetrammine complex. Consequently, many highly water insoluble copper (II) salts dissolve readily in aqueous ammonium hydroxide.

Benzoin oxime forms two series of compounds which are of interest in the analysis of inorganic ions. The first series of compounds are the ones obtained from ammoniacal solution while the second series results from the interaction of benzoin oxime with strongly acidic solutions of inorganic ions.

In ammoniacal solution benzoin oxime forms water insoluble precipitates not only with copper (II) ions, but also with nickel and cobalt ions[21]. The color of the nickel salt of benzoin oxime is buff while the corresponding cobalt salt is brown. The structures of these two salts differ from the green copper salt. Benzoin oxime acts toward nickel and cobalt ions as a monovalent acid and consequently, the ratio of metal ion to organic component is 1:2[21]. The benzoin oxime salts of nickel and cobalt are not used analytically because they are generally soluble in organic solvents. They always contain adsorped reagent which cannot be removed without loss of the metal salt.

The formation of nickel and cobalt benzoin oximes is, however, of importance in the analysis of mixtures. In the presence of nickel or cobalt, copper cannot be determined from ammoniacal solutions. The results for copper are too high due to the contamination of the precipitate with nickel or cobalt. For the determination of macro quantities of copper, accurate results are obtained by precipitating the copper from an ammoniacal solution containing tartrate ions[13]. Tartrate forms soluble complexes with a great number of ions, among which are nickel, cobalt, and copper (II) ions. With benzoin oxime only the copper tartrate complex reacts. Reproducible results are secured only if a great excess of benzene oxime is avoided. This latter condition cannot be

fulfilled in the determination of micro quantities of copper. Consequently, in micro analysis the determination of copper in the presence of nickel employing benzoin oxime has to be preceeded by separation of the nickel[43]. The formation of nickel and cobalt benzoin oxime is not only deleterious in the micro determination of copper but also in colorimetric methods for the analysis of this metal. Dunleavy, Wiberly and Harley[10] describe a photometric determination of small amounts of copper using benzoin oxime as a reagent. The method consists of the chloroform extraction of copper benzoin oxime formed in an alkaline solution containing sodium tartrate. These authors found that nickel concentrations higher than 2% and/or cobalt concentrations above 0.25% produce erroneous results in the copper determination.

The gravimetry of macro quantities of copper seems not to yield very accurate results. There is a pronounced tendency for high results which can be explained by the occlusion of benzoin oxime in the copper salt. Feigl[13] recommends the washing of the dried copper benzoin oxime with warm alcohol in order to remove the excess of precipitant. Azzalin[3] makes the statement, supported by experiments, that the excess of reagent cannot be removed from the precipitate and therefore he ignites the copper salt to copper (II) oxide prior to weighing. Furman and Flagg[18] obtained consistant slightly high results in a titrimetric determination of copper. This method is based on the oxidation of the hydroxylamine salt obtained by acid hydrolysis of copper benzoin oxime. These authors noted that it is very difficult to wash the excess of reagent out of the precipitate and that this may account for the slightly high results.

Azzalin (loc. cit.) and Shik[41] observe that the determination of copper with benzoin oxime is unsatisfactory in the presence of many foreign elements especially iron, zinc, aluminum, lead, and tin. Even in the presence

of tartrate the copper precipitate occludes these foreign materials which apparently cannot be removed by washing. In a study of coprecipitation, West and Conrad[46] showed spectrographically that chromium (III) salts are coprecipitated by copper benzoin oxime from slightly acidic solution.

The second series of compounds formed by benzoin oxime are the metallo organic compounds which are obtained in dilute mineral acid solution. Knowles[22] found that in such a medium benzoin oxime yields insoluble salts with molybdate, tungstate, vanadate, chromate and palladium (II). In the same medium columbate, tantalate and gold (III) are partially precipitated by this reagent. The precipitates obtained with molybdate, tungstate, and vanadate are of different constitution than the copper or nickel benzoin oximes. Analysis established that the ratio of metal to organic precipitant is 1:3 and Feigl[12] considers these precipitates as esters of the reagent with the acidic metal oxides or possibly as heteropolyacids. The precipitates obtained are not analytically pure and must be ignited prior to weighing. In this case benzoin oxime serves merely as a separating agent. The composition of the salts of benzoin oxime with columbate, tantalate, chromate, palladium (II) and gold (III) has not been established. In neutral solution the palladium salt has a constitution corresponding to the nickel benzoin oxime[21]. Chromate is reduced by benzoin oxime in acidic solution with the formation of a brown precipitate. Several methods for the determination of molybdate in a variety of materials have been recommended[44].

The present investigation was undertaken with the following objectives in mind:

a) Extend the study of the "copper specific" grouping, -C(NOH)-C(OH)<, to compounds not previously studied.

b) Study the behavior of copper (II) acyloin oximes toward various amines in the hope of finding an explanation for the unusual behavior of these copper salts.

c) Analytical study of the compounds synthesized. It was hoped that by employing water soluble acyloin oximes, reagents could be obtained which would be superior to benzoin oxime.

The approach to the problem was to synthesize some acyloin oximes and to study the behavior of their copper salts toward various amines. The amines selected form with copper (II) ions bonds of varying strength. It was felt that solubility of copper (II) salts of acyloin oximes might occur in some amines which are not only solvents for the respective acyloin oxime, but in addition can coordinate to copper (II) ions. As a matter of fact, pyridine and its homologues are solvents for some of the copper (II) salts of acyloin oximes. It was found that ethylenediamine, which forms a chelate with copper (II) ions, bis-ethylenediamine copper (II) ion, is an excellent solvent for all copper (II) salts of the acyloin oximes investigated.

As can be seen from Table I, Feigl and coworkers investigated only aliphatic or aromatic acyloin oximes. It was thought that the study of mixed, i.e. aliphatic and aromatic, acyloin oximes would be of interest. Strictly speaking these compounds are not acyloins, but are classified as ketols. However, they contain the same functional grouping as the acyloins. Two representatives of this class, α-hydroxyacetophenone oxime and α-hydroxyisobutyrophenone oxime were prepared and studied. Both of these oximes are water soluble and were studied more thoroughly as to the possibility of their use as reagents for the quantitative determination of copper.

In addition to phenylbenzoin oxime, the study included two additional

oximes which contained the hydroxyl group bound to a tertiary carbon atom. Because the phenyl- and benzyl- derivatives of benzoin oximes yielded copper salts soluble in dilute ammonium hydroxide, there was the possibility that insolubility in aqueous ammonia resulted only from acyloin oximes which contained the hydroxyl group bound to a secondary carbon atom.

2,2'-Thenoin which has been prepared only recently[8] was included in the study because of the coordination possibility to the sulfur atom present in the ring. As will be shown, the copper (II) salt of thenoin oxime is considerably more stable than the corresponding salt of benzoin oxime. In addition the selectivity of the reaction which benzoin oxime exhibits is lost.

Table II gives the names and the formulas of the compounds which were included in this investigation.

Table II

ACYLOIN OXIMES INVESTIGATED

Name of compound	Formula of compound
Benzoin oxime	$C_6H_5-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{CH}-C_6H_5$
2,2'-Furoin oxime	$C_4H_3O-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{CH}-C_4H_3O$
2,2'-Thenoin oxime	$C_4H_3S-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{CH}-C_4H_3S$
Phenylbenzoin oxime	$C_6H_5-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{C}(C_6H_5)_2$
Methylbenzoin oxime	$C_6H_5-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{C}(CH_3)C_6H_5$
α-Hydroxyisobutyrophenone oxime	$C_6H_5-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{C}(CH_3)_2$
α-Hydroxyacetophenone oxime	$C_6H_5-\underset{\underset{HON}{\|}}{C}-\underset{\underset{OH}{\|}}{CH}_2$

EXPERIMENTAL

A - Organic Preparations.

All temperatures are uncorrected.

Benzoin oxime:

The commercially available product, supplied by City Chemical Corporation, was recrystallized from benzene; m.p. 149-150°, m.p. (lit.[4]) 150-151°.

2,2'-Furoin oxime:

Freshly distilled furfural was condensed with potassium cyanide according to the procedure of Hartman and Dickey[19]. The furoin obtained was oximated with an excess of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The furoin oxime was finally recrystallized from a mixture of absolute alcohol and petroleum ether "B"; m.p. 157-158°, m.p. (lit.[5]) 160-161°.

2,2'-Thenoin oxime:

This preparation was carried out as described by Cardon and Lankelma[8]. Freshly distilled 2-thiophenaldehyde was condensed in the presence of potassium cyanide and the thenoin obtained was oximated with an excess of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The oxime was recrystallized from absolute alcohol. The final product had a slight brown discoloration, while the above authors report a white product; m.p. 151-152°, m.p. (lit.[8]) 142-143°.

Anal. Calcd. for $C_{10}H_9NO_2S_2$: C, 50.2; H, 3.8; N, 5.9; S, 26.8. Found: C, 50.3; H, 3.9; N, 5.7; S, 26.6.

Phenylbenzoin oxime:

Phenylbenzoin was prepared by the addition of phenylmagnesium bromide to benzil according to Acree[1]. The oxime was obtained by the action of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The product was purified by crystallization from a mixture of benzene and petroleum ether "B"; m.p. 148-149.5°, m.p. (lit.[27]) 152-153°. The melting point listed in the literature refers to the β-isomer.

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.2; H, 5.7; N, 4.6. Found: C, 79.4; H, 5.9; N, 4.7.

Methylbenzoin oxime:

Methylbenzoin was synthesized following the method described by Roger[40]; methylmagnesium iodide was added to benzil. The oxime was prepared and purified in the same manner as the phenylbenzoin oxime; m.p. 121-122°, m.p. (lit.[27]) 120-121°. The melting point listed in the literature refers to the β-isomer.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.7; H, 6.3; N, 5.8. Found: C, 74.8; H, 6.4; N, 5.8.

α-Hydroxyisobutyrophenone oxime:

To one mole of phenylmagnesium bromide in 300 ml. absolute ether, contained in a 1000 ml. 3-necked flask equipped with stirrer and reflux condenser, was added slowly and with constant stirring a solution of 0.2 moles of acetone cyanohydrin in 30 ml. anhydrous ether. The action of the Grignard reagent on the acetone cyanohydrin was very rapid and a gelatinous precipitate separated out. After the addition of the cyanohydrin was completed, the reflux condenser was replaced by a distilling head provided with thermometer and downward condenser. Some of the ether was distilled, replacing it by dry

benzene and this process was continued until the temperature of the vapor reached 60°. The reaction flask was then fitted for reflux again, and under constant stirring, the mixture was refluxed for 6 hours. After standing overnight the reaction mixture was hydrolyzed by pouring it slowly into 1000 ml. ice cold 2.5 M hydrochloric acid. The layers were separated and the acidic solution was extracted with three 150 ml. portions of benzene. The benzene was distilled until the volume of the solution measured about 80 ml. This solution was transferred to a 125-ml. Claissen flask and all solvent was removed by heating on the steam bath at normal pressure and finally under reduced pressure (aspirator). The residue was distilled under vaccuum and the following fractions were collected: a) up to 90°/12mm.; b) 90-120°/12 mm.; c) 120-130°/12 mm. Fractions a) and the residue were rejected. Fraction b) was redistilled and any distillate boiling between 120-130°/12 mm. was added to fraction c). This latter fraction weighing 11.4 g. (35%) solidified when placed on ice and was partially solid at room temperature.

Blaise and Herzog[7] prepared α-hydroxyisobutyrophenone by chlorinating isobutyrophenone and hydrolyzing the intermediately produced acetyl derivative. They reported a boiling point of 125°/12 mm.

The oxime was prepared by refluxing 6 hours the ketol obtained with a filtered solution of hydroxylamine hydrochloride (6.0 g.) and potassium hydroxide (5.0 g.) in methyl alcohol (100 ml.). The product obtained was crystallized twice from a mixture of benzene and petroleum ether "B"; m.p. 114-115°, m.p. (lit.[7]) 106°.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.0; H, 7.3; N, 7.8. Found: C, 67.35; H, 7.2; N, 7.7

The acetone cyanohydrin was prepared according to the procedure of Welsh and Clemo[45].

α-Hydroxyacetophenone oxime:

α-Hydroxyacetophenone was obtained by the hydrolysis of phenacyl bromide with an aqueous suspension of barium carbonate. It was unnecessary to obtain first the acetyl derivative as recommended by Fischer and Busch[16]. The isolation and purification of the ketol was done according to the procedure recommended by Robertson and Robinson[39]. The ketol was salted out by saturating the aqueous solution with potassium carbonate and the collected product was crystallized from petroleum ether "B"; m.p. 84-85°, m.p. (lit.[39]) 85-86°.

The oxime was prepared by refluxing for 2 hours a mixture of the ketol (5 g.) in methyl alcohol (20 ml.) with a solution of hydroxylamine hydrochloride (3.0 g.) and potassium hydroxide (2.7 g.) in water (20 ml.). The mixture was extracted with five 25 ml. portions of ether and the solution dried over anhydrous sodium sulfate. The residue obtained after evaporation of the ether was crystallized from a mixture of benzene and petroleum ether "B", m.p. 60-70°. Recrystallization from water which contained some ammonium hydroxide gave a product of m.p. 69-70°, m.p. (lit.[26]) 70°.

All the above acyloin oximes prepared in this study were obtained as white crystalline solids.

B - Determination of Solubilities.

The copper salts of acyloin oximes which are formed both in acetic acid solution and ammoniacal solution were tested for their solubilities in a series of amines. The solubility determinations were performed in the following manner: To ten drops of the acyloin oxime solution contained in a test tube, two drops of the acidic or ammoniacal copper (II) solution were added. After the addition of 1 ml. of water and thorough shaking, the mixture was centrifuged. The residue obtained was suspended in 1 ml. of 95% alcohol and the suspension separated by centrifugation. To the drained residue, 1-2 ml. of the amine was added and the mixture homogenized by shaking. After standing for a few minutes, the mixture was centrifuged again.

Solubility terms used in this study: A copper salt was designated as "insoluble" when the supernatent amine was either colorless or so faintly colored as to make a decision difficult. A copper salt was designated as "slightly soluble" (sl. sol.) when the supernatent amine was distinctly colored, but no change in the amount of solid could be observed. A copper salt was designated as "partly soluble" (partly sol.) when a noticeable quantity of the solid dissolved. A copper salt was designated as "soluble" when no noticeable amount of solid remained undissolved.

The following solutions were employed in this study:

1) Acidic copper (II) solution: 0.1 M copper (II) acetate (c.p. grade) in 0.5 M acetic acid. pH of this solution was 2.7.

2) Ammoniacal copper (II) solution: 0.1 M copper (II) sulfate (c.p. grade) in 1.0 M ammonium hydroxide. pH of this solution was 9.8.

3) Acyloin oxime solutions: 0.1 M solution of the acyloin oxime in 95% ethyl alcohol.

The amines employed were either c.p. grade or purified by distillation. Where discoloration of the c.p. grade amine had occured they were also distilled. The following list gives the sources of the materials as well as the boiling ranges of the purified amines:

Ammonium hydroxide: 27% solution in water. Baker's Analyzed.

Methylamine: 25% solution in water. Eastman Kodak 527.

Ethylamine: 33% solution in water. Eastman Kodak 506.

Isopropylamine: Eastman Kodak 875.

Aniline: Eastman Kodak 25, redistilled. Boiling point of fraction: 184-185°.

Ethylenediamine: 95-100%, Eastman Kodak 1915.

Diethylamine: The Matheson Co. 2572.

Piperidine: Eastman Kodak P-687. The product was dried over solid potassium hydroxide and distilled. Boiling point of fraction: 105-107°.

Methylaniline: Eastman Kodak 353, redistilled. Boiling point of fraction: 195-196°.

Dimethylaniline: Eastman Kodak 97.

Triethylamine: Eastman Kodak 616.

Pyridine: Baker's Analyzed.

α-Picoline: Eastman Kodak P-209, redistilled. Boiling point of fraction: 127-130°.

γ-Picoline: Eastman Kodak 2732, redistilled. Boiling point of fraction: 143-145°.

Quinoline: Eastman Kodak P-218. The product was dried over solid potassium hydroxide and distilled. Boiling point of fraction: 234-235°.

"Versene": 0.2 M aqueous solution of disodium salt of ethylenediamine

tetraacetic acid. The disodium salt used was supplied by the Alrose Chemical Co. under the trade name of "Sequestrene NA2".

The colors of the copper salts dissolved in the amines were usually green, varying from a yellow- green to a deep grass-green. Exceptions were the solution colors in ammonium hydroxide, methylamine, ethylenediamine, and versene. In these instances the colors observed were blue, indicating the formation of the respective copper (II) ammine complexes.

Table III summarizes the results obtained.

Table III

SOLUBILITY OF COPPER SALTS OF ACYLOIN OXIMES IN DIFFERENT AMINES

Amine	Cu-Benzoin oxime		Cu-Thenoin oxime	
	acetic acid solution	ammoniacal solution	acetic acid solution	ammoniacal solution
Ammonium hydroxide	sl. sol.	sl. sol.	sl. sol.	sl. sol.
Methylamine	sl. sol.	sl. sol.	sl. sol.	sl. sol.
Ethylamine	sl. sol.	sl. sol.	insoluble	insoluble
Isopropylamine	sl. sol.	sl. sol.	insoluble	insoluble
Aniline	insoluble	insoluble	insoluble	insoluble
Ethylenediamine	soluble	soluble	soluble	soluble
Diethylamine	sl. sol.	sl. sol.	insoluble	insoluble
Piperidine	insoluble	insoluble	insoluble	insoluble
Methylaniline	sl. sol.	insoluble	insoluble	insoluble
Dimethylaniline	sl. sol.	insoluble	insoluble	insoluble
Triethylamine	insoluble	insoluble	insoluble	insoluble
Pyridine	soluble	partly sol.	insoluble	insoluble
α-Picoline	soluble	partly sol.	insoluble	insoluble
β-Picoline	soluble	partly sol.	insoluble	insoluble
Quinoline	soluble	partly sol.	insoluble	insoluble
"Versene"	partly sol.	partly sol.	partly sol.	sl. sol.

Table III (contd.)

Amine	Cu-Furoin oxime		Cu-Phenylbenzoin oxime	
	acetic acid solution	ammoniacal solution	acetic acid solution	ammoniacal solution
Ammonium hydroxide	soluble	soluble	soluble	soluble
Methylamine	partly sol.	partly sol.	soluble	soluble
Ethylamine	partly sol.	insoluble	soluble	soluble
Isopropylamine	partly sol.	insoluble	soluble	soluble
Aniline	insoluble	insoluble	soluble	soluble
Ethylenediamine	soluble	soluble	soluble	soluble
Diethylamine	insoluble	insoluble	soluble	soluble
Piperidine	insoluble	insoluble	soluble	soluble
Methylaniline	insoluble	insoluble	soluble	soluble
Dimethylaniline	insoluble	insoluble	soluble	soluble
Triethylamine	insoluble	insoluble	soluble	soluble
Pyridine	partly sol.	partly sol.	soluble	soluble
α-Picoline	partly sol.	partly sol.	soluble	soluble
γ-Picoline	partly sol.	partly sol.	soluble	soluble
Quinoline	partly sol.	partly sol.	soluble	soluble
"Versene"	partly sol.	partly sol.	partly sol.	partly sol.

Table III (contd.)

Amine	Cu-Methylbenzoin oxime		Cu- α-Hydroxyisobutyrophenone oxime	
	acetic acid solution	ammoniacal solution	acetic acid solution	ammoniacal solution
Ammonium hydroxide	partly sol.	sl. sol.	soluble	partly sol.
Methylamine	insoluble	insoluble	insoluble	insoluble
Ethylamine	insoluble	insoluble	sl. sol.	insoluble
Isopropylamine	sl. sol.	insoluble	insoluble	insoluble
Aniline	sl. sol.	insoluble	partly sol.	insoluble
Ethylenediamine	soluble	soluble	soluble	soluble
Diethylamine	insoluble	insoluble	insoluble	insoluble
Piperidine	sl. sol.	sl. sol.	sl. sol.	insoluble
Methylaniline	insoluble	insoluble	insoluble	insoluble
Dimethylaniline	insoluble	insoluble	sl. sol.	insoluble
Triethylamine	insoluble	insoluble	insoluble	insoluble
Pyridine	partly sol.	insoluble	partly sol.	sl. sol.
α-Picoline	partly sol.	insoluble	partly sol.	sl. sol.
γ-Picoline	partly sol.	insoluble	partly sol.	sl. sol.
Quinoline	partly sol.	insoluble	partly sol.	sl. sol.
"Versene"	partly sol.	sl. sol.	partly sol.	partly sol.

Table III (contd.)

Amine	Cu-α-Hydroxyacetophenone oxime	
	acetic acid solution	ammoniacal solution
Ammonium hydroxide	sl. sol.	partly sol.
Methylamine	sl. sol.	partly sol.
Ethylamine	insoluble	partly sol.
Isopropylamine	insoluble	partly sol.
Aniline	insoluble	insoluble
Ethylenediamine	soluble	soluble
Diethylamine	insoluble	insoluble
Piperidine	insoluble	sl. sol.
Methylaniline	insoluble	insoluble
Dimethylaniline	insoluble	insoluble
Triethylamine	insoluble	insoluble
Pyridine	partly sol.	sl. sol.
α-Picoline	sl. sol.	sl. sol.
γ-Picoline	partly sol.	sl. sol.
Quinoline	partly sol.	sl. sol.
"Versene"	partly sol.	soluble

C - Qualitative Analytical Studies.

The reactivity of the acyloin oximes towards metal ions was tested in the conventional manner of spot test analysis. To one drop of the solution of the metal ion in the depression of a white spot plate was added one drop of the solution of the conditioning agent followed by one drop of the reagent solution. Because most precipitates produced were white, the test was repeated in a black spot plate in case the formation of a precipitate could not be easily discerned against the white background.

The following list gives the metal ions tested in this study: Ag (I), Al (III), As (III), Au (III), Ba (II), Be (II), Bi (III), Ca (II), Cd (II), Ce (IV), Ce (III), Co (II), Cr (III), CrO_4^{-2}, Cs (I), Cu (II), Fe (III), Fe(II), In (III), Ir (IV), Hg (II), Hg_2 (II), K (I), La (III), Li (I), Mg (II), Mn (II), MoO_4^{-2}, Na (I), NH_4 (I), Ni (II), Pb (II), Pd (II), Pt (IV), Rb (I), Rh (III), Ru (III), Sb (III), Sn (IV), Sn (II), Sr (II), Ti (III), Th (IV), Tl (I), UO_2 (II), VO_3^{-1}, WO_4^{-2}, Zn (II), ZrO (II).

The concentration of the metal ion solutions employed was 10 mg. of metal ion per milliliter. The Au (III), Ir (IV), Rh (III), Ru (III), and Pt(IV) solutions contained only 5 mg. of metal ion per milliliter.

As conditioning agents the following solutions were used:

1) Sulfuric acid: 6 M solution.
2) Sodium acetate: 3 M solution.
3) Ammonium hydroxide: 3 M solution.
4) Ammonium hydroxide and ammonium nitrate: 1 M solution NH_4NO_3 in 3 M NH_4OH.
5) Sodium citrate: 1 M solution.
6) Sodium malonate: 1 M solution.
7) Sodium oxalate: Saturated solution, approximately 0.25 M.

8) Sodium potassium tartrate: 1 M solution.

Tables IV to X summarize the results obtained in this study. In the cases where the conditioning agents alone gave a precipitate with the metal ion, compound formation with the respective reagents was only noted if an easily detectable color change occured. Phenylbenzoin oxime is very insoluble in water and consequently a white precipitate was always obtained. A reaction was reported only when a precipitate was obtained which was distinguishable from that of this reagent.

The sensitivities of the reactions between the acyloin oximes and copper (II) ions were determined by bringing together in the depression of a white spot plate a drop of the conditioned copper (II) solution with a drop of the alcoholic solution of the acyloin oxime. As conditioning agents the following solutions were employed:

1) Ammonium hydroxide: 3 M solution.

2) Sodium acetate: 3 M solution.

3) Pyridine: 1 M aqueous solution.

The volume of the copper (II) test solution was in all cases 0.05 ml.

Table XI reproduces the sensitivities (limit of identification) of the reactions between copper (II) ions and acyloin oximes.

Table IV

REACTIONS OF METAL IONS WITH BENZOIN OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, brown; MoO_4^{-2}, white; VO_3^{-1}, yellow; WO_4^{-2}, white.
Sodium acetate	Ag(I), white; Au(III), yellow; Cd(II), white; Ce(IV), yellow; Co(II), tan; Cr(III), grey blue; Cu(II), green; Fe(III), brown; Fe(II), brown; Hg(II), white; Ni(II), buff; Pb(II), white; Pd(II), yellow; Ru(III), black; Th(IV), white; UO_2(II), yellow; Zn(II), white; ZrO(II), white.
Ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Ni(II), buff; Zn(II), white.
Ammonium hydroxide and ammonium nitrate	Co(II), tan; Cu(II), green; Ni(II), buff.
Sodium citrate and ammonium hydroxide	Co(II), tan; Cu(II), green; Ni(II), buff; Pb(II), white; UO_2(II), yellow.
Sodium malonate and ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Ni(II), buff; Zn(II), white.
Sodium oxalate and ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Ni(II), buff; Zn(II), white.
Sodium potassium tartrate and ammonium hydroxide	Co(II), tan; Cu(II), green, Ni(II), buff; UO_2(II), yellow.

Table V

REACTIONS OF METAL IONS WITH 2,2'-FUROIN OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, green coloration (reduction); MoO_4^{-2}, white; VO_3^{-1}, yellow coloration; WO_4^{-2}, greenish coloration.
Sodium acetate	Ag(I), white; Au(III), reduction; Ce(IV), yellow coloration; Co(II), brown; Cr(III), bluish green; Cu(II), green; Fe(III), brown; Fe(II), brown; Hg(II), white; Ni(II), tan; Pb(II), white; Pd(II), yellow; Ru(III), deep purple coloration; UO_2(II), yellow coloration; Zn(II), white.
Ammonium hydroxide	Ce(IV), $Ce(OH)_4$ turns yellow; Co(II), brown; Cu(II), green; Ni(II), tan.
Ammonium hydroxide and ammonium nitrate	Co(II), brown; Cu(II), green; Ni(II), tan.
Sodium citrate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), tan; Pb(II), white.
Sodium malonate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), tan.
Sodium oxalate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), tan.
Sodium potassium tartrate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), tan.

Table VI

REACTIONS OF METAL IONS WITH 2,2'-THENOIN OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, brown; MoO_4^{-2}, yellowish white; VO_3^{-1}, tan; WO_4^{-2}, yellowish white.
Sodium acetate	Ag(I), white; Au(III), yellow; Bi(III), white; Cd(II), white; Ce(IV), yellow brown; Co(II), tan; Cu(II), green; Fe(III), red brown; Fe(II), red brown; Hg(II), white; Ni(II), orange; Pb(II), white; Pd(II), yellow; Ti(III), yellowish coloration; Th(IV), white; UO_2(II), yellow; Zn(II), white; ZrO(II), white.
Ammonium hydroxide	Cd(II), white; Ce(IV), $Ce(OH)_4$ ppt. turns yellow; Co(II), tan; Cu(II), green; Ni(II), orange; Tl(I), white; Zn(II), white.
Ammonium hydroxide and ammonium nitrate	Cd(II), white; Co(II), tan; Cu(II), green; Ni(II), orange; Ti(III), $Ti(OH)_3$ ppt. turns yellow; Zn(II), white.
Sodium citrate and ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Fe(III), yellow turbidity; Fe(II), yellow brown; In(III), white; Mn(II), brown coloration; Ni(II), orange; Pb(II), white; Zn(II), white.
Sodium malonate and ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Fe(II), yellow brown; Mn(II), brown; Ni(II), orange; Zn(II), white.
Sodium oxalate and ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Fe(II), yellow brown; Mn(II), brown; Ni(II), orange; Zn(II), white.
Sodium potassium tartrate and ammonium hydroxide	Cd(II), white; Co(II), tan; Cu(II), green; Fe(III), yellow turbidity; Fe(II), yellow brown; In(III), white; Mn(II), brown; Ni(II), orange; Pb(II), white; Zn(II), white.

Table VII

REACTIONS OF METAL IONS WITH METHYLBENZOIN OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, brown; MoO_4^{-2}, white; VO_3^{-1}, yellow; WO_4^{-2}, white.
Sodium acetate	Ag(I), white; Au(III), yellow; Ce(IV), yellowish white; Co(II), pink; Cr(III), grey blue; Cu(II), green; Fe(III), brown; Fe(II), yellow; Hg(II), white; Ni(II), buff; Pd(II), yellow; Pb(II), white; Ru(III), dark brown; Th(IV), white; UO_2(II), yellow; Zn(II), white.
Ammonium hydroxide	Cd(II), white; Co(II), brown; Cu(II), green; Ni(II), buff.
Ammonium hydroxide and ammonium nitrate	Co(II), brown; Cu(II), green; Ni(II), buff.
Sodium citrate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), buff; Pb(II), white; UO_2(II), yellow.
Sodium malonate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), buff.
Sodium oxalate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), buff.
Sodium potassium tartrate and ammonium hydroxide	Co(II), brown; Cu(II), green; Ni(II), buff; UO_2(II), yellow.

Table VIII

REACTIONS OF METAL IONS WITH PHENYLBENZOIN OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, brown; MoO_4^{-2}, white; VO_3^{-1}, yellow; WO_4^{-2}, white.
Sodium acetate	Ag(I), white; Cd(II), white; Ce(IV), yellow; Ce(III), white; Co(II), pink; Cr(III), blue green; Cu(II), green; Fe(III), brown; Fe(II), yellow; Hg(II), white; Ni(II), buff; Pb(II), white, Pd(II), yellow; Ru(III), dark brown coloration; Tl(I), white; UO_2(II), yellow; Zn(II), white.
Ammonium hydroxide	Ba(II), white; Ca(II), white; Cd(II), white; Co(II), brown; Cu(II), green; Ni(II), buff; Sr(II), white; Tl(I), white; Zn(II), white.
Ammonium hydroxide and ammonium nitrate	Ba(II), white; Ca(II), white; Co(II), brown; Cu(II), green; Ni(II), buff; Sr(II), white; Zn(II), white.
Sodium citrate and ammonium hydroxide	Co(II), pink; Cu(II), green; Ni(II), buff; Pb(II), white; Ti(III), white; Th(IV), white; Tl(I), white; UO_2(II), yellow; Zn(II), white.
Sodium malonate and ammonium hydroxide	Cd(II), white; Co(II), pink; Cu(II), green; Ni(II), buff; Tl(I), white; Zn(II), white.
Sodium oxalate and ammonium hydroxide	Cd(II), white; Co(II), pink; Cu(II), green; Ni(II), buff; Tl(I), white; Zn(II), white.
Sodium potassium tartrate and ammonium hydroxide	Co(II), pink; Cu(II), green; Mn(II) light tan; Ni(II), buff; Pb(II), white; Ti(III), white; Th(IV), white; Tl(I), white; UO_2(II), yellow; Zn(II), white.

Table IX

REACTIONS OF METAL IONS WITH α-HYDROXYISOBUTYROPHENONE OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, brown; VO_3^{-1}, purple coloration; WO_4^{-2}, white.
Sodium acetate	Cu(II), green; Pd(II), yellow.
Ammonium hydroxide	Cu(II), green; Ni(II), buff coloration.
Ammonium hydroxide and ammonium nitrate	Cu(II), green.
Sodium citrate and ammonium hydroxide	Cu(II), green coloration.
Sodium malonate and ammonium hydroxide	Cu(II), green.
Sodium oxalate and ammonium hydroxide	Cu(II), green.
Sodium potassium tartrate and ammonium hydroxide	Cu(II), green.

Table X

REACTIONS OF METAL IONS WITH α-HYDROXYACETOPHENONE OXIME

Conditioning agent	Reacting ions and color of precipitates
Sulfuric acid	CrO_4^{-2}, green coloration (reduction); VO_3^{-1}, dark blue coloration (reduction).
Sodium acetate	Cu(II), green; Pd(II), yellow.
Ammonium hydroxide	Cu(II), green; Ni(II), buff.
Ammonium hydroxide and ammonium nitrate	Cu(II), green.
Sodium citrate and ammonium hydroxide	None
Sodium malonate and ammonium hydroxide	Cu(II), green.
Sodium oxalate and ammonium hydroxide	Cu(II), green.
Sodium potassium tartrate and ammonium hydroxide	Cu(II), green.

Table XI

SENSITIVITIES OF COPPER(II)-ACYLOIN OXIME REACTIONS

Acyloin oxime	Limit of identification of copper (μg)		
	Ammonium hydroxide	Sodium acetate	Aqueous pyridine
Benzoin oxime	8	2	1.5
2,2'-Furoin oxime	15	8	1.5
2,2'-Thenoin oxime	2	2	1.5
Phenylbenzoin oxime	20	20	5
Methylbenzoin oxime	2	1	1
α-Hydroxyisobutyrophenone oxime	2	1	1
α-Hydroxyacetophenone oxime	1	1	0.5

D - Quantitative Analytical Studies.

Because of the water solubility of α-hydroxyacetophenone oxime and α-hydroxyisobutyrophenone oxime these two compounds were tested as precipitants for copper. The determination procedure was as follows:

A weighed amount of electrolytic copper wire was dissolved in 5 ml. of 6 M nitric acid. The resultant solution was diluted with water to 200 ml. and concentrated ammonium hydroxide added drop by drop until a permanent blue color was obtained. An excess of 1 ml. of concentrated ammonium hydroxide was added. The solution was heated to boiling, the flame removed, and a slight excess of the alcoholic reagent solution (α-hydroxyacetophenone oxime: 1 g. of compound in 100 ml. of 95% ethyl alcohol; α-hydroxyisobutyrophenone oxime: 2 g. of compound in 100 ml. of 95% ethyl alcohol) was slowly poured into the hot copper solution while stirring it constantly. The precipitate was digested for 30 minutes on a hot plate and then filtered through a tared sintered glass crucible (medium fine). The copper salt was washed six times with boiling hot water and dried to constant weight at 125-130°. At this temperature constant weight of the precipitate was obtained within one hour.

The filtration of the copper salts are fairly expeditious and very satisfactory. However, the precipitates have a tendency to adhere to the walls of the beaker and the last part of the precipitate has to be removed with the aid of a rubber policeman.

In acetic acid solution the determination procedure was slightly modified. To the acidic copper (II) nitrate solution, sodium hydroxide (2 M) was added drop by drop until a permanent precipitate was obtained. This precipitate was dissolved by the dropwise addition of 6 M acetic acid. To assure an acidic reaction a few drops of acetic acid were added in excess. The pH of the

solution obtained was ascertained with pHydron paper and established to be between 4 and 5.

The gravimetric factors for copper α-hydroxyacetophenone oxime and copper α-hydroxyisobutyrophenone oxime are : 0.2987, log 0.47530 - 1 and 0.2639, log 0.42150 - 1, respectively.

Table XII summarizes the results obtained by determining copper with α-hydroxyacetophenone oxime and α-hydroxyisobutyrophenone oxime. With the latter reagent copper was also determined in the presence of nickel (II) and cobalt (II) ions.

Analysis of copper salts.

In addition to the copper salts of α-hydroxyacetophenone oxime and α-hydroxyisobutyrophenone oxime the copper salts of methylbenzoin oxime and thenoin oxime were analyzed in identical fashion. A measured amount of copper was precipitated with excess reagent and the copper salt obtained weighed after drying. With methylbenzoin oxime and thenoin oxime, the excess reagent had to be removed by washing with hot ethyl alcohol.

Table XIII reproduces the results obtained. Although the amounts of copper methylbenzoin oxime and copper thenoin oxime obtained are somewhat high, there is little doubt that the ratio of copper to oxime is in all cases 1:1.

Table XII

GRAVIMETRIC DETERMINATION OF COPPER

A - With α-Hydroxyacetophenone oxime

Conditioning agent	Foreign ions present	Weight of copper (grams) found	present
Ammonium hydroxide	None	.0244	.0244
		.0255	.0253
		.0481	.0475
		.0543	.0536
		.0656	.0652

B - With α-Hydroxyisobutyrophenone oxime

Conditioning agent	Foreign ions present	Weight of copper (grams) found	present
Ammonium hydroxide	None	.0107	.0106
		.0120	.0118
		.0319	.0317
		.0324	.0325
		.0603	.0605
		.0655	.0657
		.0819	.0820
		.1292	.1290
	Nickel (II)	.0267	.0247
		.0271	.0252
Acetic acid	None	.0189	.0186
		.0256	.0252
		.0309	.0306
		.0503	.0499
	Nickel (II)	.0223	.0217
	Cobalt (II)	.0233	.0224

Table XIII

ANALYSIS OF COPPER SALTS OF ACYLOIN OXIMES

Acyloin oxime	Weight of copper (grams)	Weight of copper salt found (grams)	Weight of copper salt calculated (grams)
2,2'-Thenoin oxime	.0244	.1185	.1155
	.0251	.1215	.1188
Methylbenzoin oxime	.0278	.1337	.1325
	.0283	.1378	.1349
α-Hydroxyisobutyrophenone oxime	.0317	.1209	.1201
	.0325	.1227	.1231
α-Hydroxyacetophenone oxime	.0244	.0817	.0817
	.0253	.0852	.0847

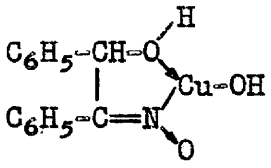
DISCUSSION OF RESULTS AND CONCLUSIONS

The present investigation extended the study of the atomic grouping, $-C(NOH)-C(OH)<$, characteristic of acyloin oximes to four compounds not previously examined; i.e. 2,2'-thenoin oxime, methylbenzoin oxime, α-hydroxyisobutyrophenone oxime, and α-hydroxyacetophenone oxime. These compounds showed the same reactivity towards copper (II) ions as benzoin oxime, the most readily available compound containing the above atomic grouping. All compounds form green, water insoluble copper salts which contain bivalent copper and in which the ratio of copper to acyloin oxime is 1:1.

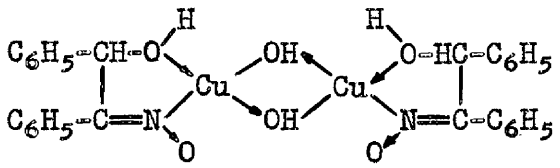
The behavior of the copper salts of these acyloin oximes as well as the copper salts of benzoin oxime, 2,2'-furoin oxime and phenylbenzoin oxime was tested towards various amines. As can be seen from Table III, only ethylenediamine is a solvent for all copper salts of acyloin oximes. From the solution color (blue) it can be assumed that the salts are decomposed under formation of bis-ethylenediamine copper (II) ion. This chelate is exceedingly stable and therefore the decomposition of the copper acyloin oxime by ethylenediamine is not too surprising. Rather unusual, however, is the behavior of the acyloin oximes towards ammonium hydroxide and methylamine. Both amines form very strong bonds with copper (II) ions, yet the copper salts of acyloin oximes are not generally soluble in these two reagents. As was elaborated in the introduction, this unusual behavior prompted Feigl[13] to postulate the copper salts of acyloin oximes as inner complex salts. The slight solubility of the copper salt of α-hydroxyacetophenone oxime and of the copper salt of α-hydroxyisobutyrophenone oxime which is formed in ammoniacal solution seems to afford evidence against this postulate. In these cases copper could coordinate to only one phenyl radical giving the metal a coordination number of 3 which is

very unlikely for divalent copper.

The question arises as to the structure of the copper salts of acyloin oximes. Dubsky and Langer[9] ascribe to the copper benzoin oxime the structure of a basic salt (a) which is considered to immediately dimerize to the structure (b).



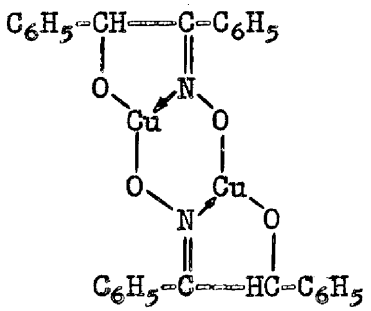
(a)



(b)

This structure, however, does not agree with the analytical results, for it would contain one molecule of water while the analysis of the salt corresponds to an anhydrous salt.

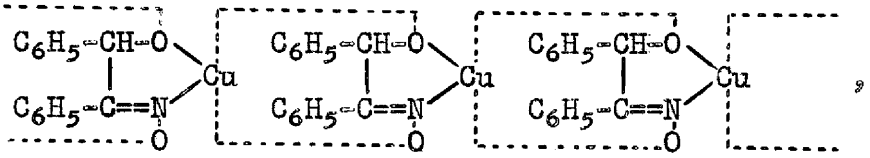
Langer[24] postulates a dimeric copper benzoin oxime of the following structure:



This structure calls for a coordination number of 3 for divalent copper and in addition the oxime group would not react in the nitrone form,  , but in the usual oxime form, =N-OH. This is in contrast to the behavoir of the oxime group in dioximes. Also the β-isomer of benzoin oxime does not form a green, water insoluble copper salt[12] and, therefore, it can be assumed that in benzoin oxime the nitrone form is the reactive form of the oxime group.

Ray and Sen[38] conclude from magnetic susceptibility studies that the

copper in the benzoin oxime compound has a coordination number of 4. They assume for this copper salt an unending chain structure,



similar to the structure of anhydrous palladium (II) chloride, and state that the configuration may have either a cis or trans arrangement of oxygen and nitrogen atoms around the central copper atom.

From steric considerations a chain structure similar to anhydrous palladium (II) chloride seems rather unlikely. However, the behavior of the copper salts of acyloin oximes can best be explained on the assumption of a polymeric structure.

If we assume a polymeric structure, the insolubility in ammonia can be explained without recourse to coordination to phenyl radicals or multimember aliphatic radicals. The central copper atom would be shielded from an attack by the ammonia molecule by hydrophobic groups such as phenyl or multimembered aliphatic radicals. Then also the solubility of the copper salt of phenylbenzoin oxime and benzylbenzoin oxime could be explained by the inability of these acyloin oximes to form such polymers because of the size of the organic component. From the reactivity of the acyloin oximes towards different metal ions (Tables IV to X) as well as from the determination of the sensitivity of the copper acyloin oxime reaction (Table XI), it can be concluded that the copper salt of phenylbenzoin oxime has a somewhat different structure than the copper salts of the other acyloin oximes studied.

In favor of a polymeric structure are also the solubility relationships of the copper salts of acyloin oximes. If the copper salt of benzoin oxime would have the structure proposed by Feigl, coordination of the copper

atom to the phenyl radicals, this compound could be expected to be freely soluble in such solvents as benzene, chloroform, etc. This, however is not the case.

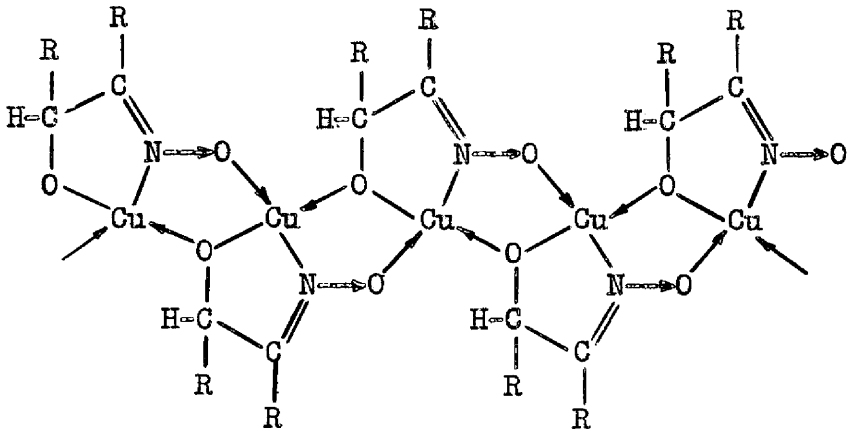
For dissolution to occur the solvent must interact with the solute forming solvated molecules in which the solvent molecules probably are held to the solute molecules by van der Waals' forces. The solvent molecules of this "complex" become then the centers of interaction with the molecules of the bulk of the solvent and dissolution results.

If the molecule which is to be dissolved contains both hydrophilic and hydrophobic groups, dissolution does not usually occur in either hydrophilic or hydrophobic solvents but may often occur in a mixture of these two types of solvents. An example is afforded by the behavior of heavy metal salts of long chain fatty acids which are neither soluble in hydrocarbon solvents such as chloroform nor solvents containing hydroxyl groups such as glycols. However, these metal salts are freely soluble in mixtures of glycols and chloroform. This has been experimentally verified by Palit and McBain[30]. If a compound possesses both hydrophobic and hydrophilic groupings, it can be expected to be a solvent for the type of molecule under discussion. Palit[29] found that phenol, creosol, methyl alcohol, etc. which do fulfill this requirement are solvents for metal soaps.

On the basis of the above considerations one might expect dissolution of copper acyloin oximes in solvents which can coordinate to copper and simultaneously are good solvents for the organic part of the molecule. Pyridine and its homologues satisfy these two criteria and as can be seen from Table III these compounds are the best solvents for the copper salts studied. But even in these solvents the copper salts are only moderately soluble.

The strength of the copper-acyloin oxime bond is of paramount importance in determining the chemical and physical properties of the copper salt. The strength of the bond is dependent upon the electron density of the donor groups and, therefore, individual differences in the behavior of the copper salts can be expected.

A structure which seems to fit all available experimental data is given below.



This polymeric structure would explain why the copper salts of aliphatic acyloin oximes become insoluble in dilute ammonia when the aliphatic radical has at least four carbon atoms. It also is in agreement with the solubility relations of the copper salt of fructose oxime.

Proof for or against a polymeric structure could be obtained by molecular weight determinations if a suitable solvent were available. None of the solvents used in this study are applicable because of too limited solubility or the possibility of compound formation. Although the solution color of copper acyloin oximes in pyridine is green, this does not exclude the possibility of a pyridine addition product. Although the usual color of copper-pyridine complexes is blue, numerous green compounds between copper and pyridine have been described in the literature[6].

The compounds studied were not found superior to benzoin oxime as quantitative reagents. Because α-hydroxyisobutyrophenone oxime and α-hydroxyacetophenone oxime are water soluble, they were expected to remove the main drawback of benzoin oxime; i.e. occlusion of reagent in the copper precipitate. However, it was found that α-hydroxyacetophenone oxime gave consistantly high results for copper and, therefore, was condemmed as a quantitative reagent for this metal. α-Hydroxyisobutyrophenone oxime gave good results for pure copper in pure ammoniacal solutions. Nickel ions, however, were found to interfer. In the presence of tartrate ions, the copper acyloin oxime did not form and tartrate could not be used as a masking agent. In acetic acid solution the results of the copper determination were all high and furthermore nickel and cobalt ions are coprecipitated.

As qualitative reagents for copper, α-hydroxyacetophenone oxime and α-hydroxyisobutyrophenone oxime are superior to benzoin oxime not only because of increased sensitivity but also because of lack of interferences as can be seen in Tables IX to XI.

SELECTED BIBLIOGRAPHY

1) Acree, S.F. "Some Syntheses with Phenylsodium and Alkylmagnesium bromides," Ber., 37: 2753-64 (1904)

2) Alexander, E.R. Principles of Ionic Organic Reactions. New York: John Wiley and Sons, 1950. P. 35 ff.

3) Azzalin, E. "The Method of Feigl for the Determination of Copper," Ann. chim. applicata, 15: 373-377 (1925); C.A., 20: 1041 (1925)

4) Beilsteins Handbuch der Organischen Chemie. Fourth edition. Berlin: Verlag von Julius Springer, 1935. VIII, P. 175

5) _____. Ibid. XIX, P. 205

6) _____. Ibid. XX, P. 191-192

7) Blaise, E.E. and Herzog, "Constitution of the Chlorides of Acetylated α-Hydroxyacids," Compt. rend., 184: 1332-1333 (1927)

8) Cardon, S.Z. and Lankelma, H.P. "The Acyloin Condensation of 2-Thiophenaldehyde," J. Am. Chem. Soc., 70: 4248-4249 (1948)

9) Dubsky, J.V. and Langer, A. "The Systematic Synthesis of Atomic Groupings in Analytical Chemistry. IV. The Atomic Arrangement Necessary for the Specific Detection of Copper," Chem. Obzor., 13: 178-184 (1939); C.A., 33: 7690 (1939)

10) Dunleavy, R.A., Wiberly, S.E. and Harley, J.H. "Rapid Photometric Determination of Copper in Ferrous Alloys," Anal. Chem., 22: 170-172 (1950)

11) Feigl, F. Chemistry of Specific, Selective, and Sensitive Reactions. Translated by R.E. Oesper. New York: Academic Press Inc., 1949. P. 267

12) _____. Ibid. P. 269

13) Feigl, F. "A New Special Reagent and a New Method for the Determination of Copper," Ber., 56: 2083-2085 (1923)

14) Feigl, F., Sicher, G. and Singer, O. "The Copper-affine Activity of the Atomic Grouping >C(OH)-C(NOH)- . A Contribution to the Knowledge of the Relationships between the Atomic Groupings and Specific Affinity," Ber., 58: 2294-2303 (1925)

15) Fieser, L.F. and Fieser, M. Organic Chemistry. Second Edition. Boston: D.C. Heath and Company, 1950. P. 747

16) Fischer, O. and Busch, M. "A New Class of Fluorescent Dyes of the Quinoline Series III," Ber. 24: 2679-2683 (1891)

17) de Forcradn, M. "The Composition of Gas Hydrates," Compt. rend., 135: 959 (1902)

18) Furman, N.H. and Flagg, J.F. "Studies of Organic Reagents and Methods Involving Their Use," Ind. Eng. Chem. Anal. Ed., 12: 738-740 (1940)

19) Hartman, W. W. and Dickey, J. B. "The Preparation of Furil," J. Am. Chem. Soc., 55: 1228-29 (1933)

20) Hofmann, K.A. and Küspert, F. "Compounds of Hydrocarbons with Metal Salts," Z. anorg. Chem., 15: 204-207 (1897); compare also Ber., 39: 339-344 (1906)

21) Jennings, J.S., Sharratt, E. and Wardlaw, W. "Compounds of α-Benzoin Oxime with Bivalent Metals," J. Chem. Soc., 1935: 818-822

22) Knowles, H.B. "Use of α-Benzoin Oxime in the Determination of Molybdenum," Bur. Standards J. Res., 9: 1-7 (1932)

23) Koreman, I.M. and Ditset, L.E. "Fractional Reaction for Copper," Zavodskaya Lab., 10: 493 (1941); C.A., 35: 7870 (1941)

24) Langer, A. "Amperometric Titration of Copper with Benzoin Oxime," Ind. Eng. Chem. Anal. Ed., 14: 283-285 (1942)

25) Martell, A.E. and Calvin, M. Chemistry of the Metal Chelate Compounds. New York: Prentice Hall, Inc., 1952. p. 16

26) Meyer, V. and Naegeli, E. "The Oxoctenol," Ber., 16: 1622-1624 (1883)

27) Oryekhov, A. and Tiffeneau, M. "The Action of the Organomagnesium Derivatives on the Isonitrosoketones. The Synthesis of Some Alcohol Oximes," Bull. Soc. Chim. [4] 41: 839-843 (1927)

28) Palin, D.E. and Powell, H.M., "The Structure of Molecular Compounds Part III. Crystal Structure of Addition Complexes of Quinol with Certain Volatile Compounds," J. Chem. Soc., 1947: 208-221

29) Palit, S.R. "The Solubility of Soaps and of Some Salts in Mixtures of Solvents one of which is of Glycolic Type," J. Am. Chem. Soc., 69: 3120-3129 (1947)

30) Palit, S.R. and McBain, J.W. "The Solubility of Heavy Metal Soaps in Co-solvent Mixtures of Chloroform and Propylene Glycol," J. Am. Oil Chemists' Soc., 24: 190-193 (1947)

31) Pauling, L. The Nature of the Chemical Bond. Second Edition. Ithaca, Cornell University Press, 1945. p. 139 ff.

32) Pfeiffer, P. Organische Molekülverbindungen. Second Edition. Stuttgart: Verlag von Ferdinand Enke, 1927. P. 209-210

33) _____. Ibid. P. 210

34) _____. Ibid. P. 211

35) _____. Ibid. P. 256

36) Pfeiffer, P. and Richarz, J. "The Constitution of Inner Complex Salts of α-Monoximes and α-Dioximes of Diketones," Ber., 61: 103-107 (1928)

37) Powell, H.M. and Rayner, J.H. "Clathrate Compound Formed by Benzene with an Ammoniacal Nickel Cyanice Complex," Nature, 163: 566-567 (1949)

38) Ray, P. and Sen, D.N. "Magneto-chemical Studies in Valency. Part VI. Bond Type and Stereochemistry of Four-coordinated Copper Complexes," J. Indian Chem. Soc., 25: 473-482 (1948)

39) Robertson, A. and Robinson, R. "Experiments on the Synthesis of Anthocyanins. Part II. The Synthesis of 3- and 7-Glucosidoxyflavylium Salts," J. Chem. Soc., 1927: 242-247; see footnote P. 244.

40) Roger, R. "The Synthesis of Glycols from Atrolactinic Acid," J. Chem. Soc., 127: 518-523 (1924)

41) Shik, I.R. "Use of α-Benzoin Oxime for the Determination of Copper," Zavodskaya Lab., 9: 542-545 (1940); C. A., 34: 7204 (1940)

42) von Stackelberg, M. "Solid Gas Hydrates," Naturwisserschaften, 36: 327-333 (1949)

43) Strebinger, R. "Copper Benzoin Oxime as a Form for Weighing in Qualitative Microanalysis," Mikrochemie, 1: 72-74 (1923)

44) Welcher, F.J. Organic Analytical Reagents. New York: D. Van Nostrand Company, 1947. III, P. 246-250

45) Welsh, K.N. and Clemo, G.R. "The Preparation of Acetonecyanohydrin," J. Chem. Soc., 1928: 2629

46) West, P.W. and Conrad, L.J. "A Comparison Study of the Coprecipitation of Cations by Organic and Inorganic Precipitants," Anal. Chim. Acta, 4: 561-565 (1950)

47) Winstein, S. and Lucas, H.J. "Coordination of Silver Ion with Unsaturated Compounds," J. Am. Chem. Soc., 60: 836-847 (1938)

VITA

Hans Albert Suter was born November 7, 1920 in Belem do Para, Brazil. In 1931 he moved to Switzerland where he continued his primary education and where he entered high school in Zurich. From 1939 to 1941 he worked as chemical assistant in Sao Paulo, Brazil. In 1941 he began working for Dr. Fritz Feigl in Rio de Janeiro, Brazil, and he continued to work there until 1946. In June 1947 he enrolled in Louisiana State University and graduated with a Bachelor of Science degree in Chemistry in June, 1949. In September, 1950 he re-entered Louisiana State University as a graduate assistant in the department of Chemistry and received the degree of Master of Science in June, 1952.

In June, 1949 he married Patricia E. Howe of Baton Rouge and they have one son, Henry Albert.

He is now a candidate for a Doctor of Philosophy degree in Chemistry.

EXAMINATION AND THESIS REPORT

Candidate: Hans Albert Suter

Major Field: Chemistry

Title of Thesis: Analytical Studies of Some Acyloin Oximes

Approved:

Philip W. West
Major Professor and Chairman

Richard J. Russell
Dean of the Graduate School

EXAMINING COMMITTEE:

J. L. E. Ericksen

Clark M. Welch

D. J. Robichaux

Lloyd W. Morris

Date of Examination:

July 29, 1953